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Electrochemical doping for lowering contact barriers in organic field effect transistors

Stefan Schaur [a], Philipp Stadler [a,*], Beatriz Meana-Esteban [a,b,c], Helmut Neugebauer [a], N. Serdar Sariciftci [a]

[a] Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University of Linz, A-4040 Linz, Austria
[b] Laboratory of Materials Chemistry and Chemical Analysis, Department of Chemistry, University of Turku, FI-20014 Åbo/Turku, Finland
[c] Turku University Centre for Materials and Surfaces (MATSURF), University of Turku, FI-20014 Åbo/Turku, Finland

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ABSTRACT

By electrochemically p-doping pentacene in the vicinity of the source-drain electrodes in organic field effect transistors the injection barrier for holes is decreased. The focus of this work is put on the influence of the p-doping process on the transistor performance. Cyclic voltammetry performed on a pentacene based transistor exhibits a reversible p-doping response. This doped state is evoked at the transistor injection electrodes. An improvement is observed when comparing transistor characteristics before and after the doping process apparent by an improved transistor on-current. This effect is reflected in the analysis of the contact resistances of the devices.

1. Introduction

Organic fused ring molecules such as pentacene excel in terms of their interesting electronic properties as thin film semiconductors with charge carrier mobilities in the range of up to 23 $cm^2 V^{-1} s^{-1}$ [1–3]. The implementation of organic small molecules as active material to organic field effect transistors (OFETs) and furthermore to complex and flexible integrated circuits (ICs) has shown great progress over the last decade [4–7]. However, fast, organic device circuits operating in MHz regime may still not be feasible with state-of-the-art organic transistors. Two major limitations are revealed addressing the comparatively low mobilities of organic disordered thin films on the one hand and contact barriers on the other hand. While optimization of deposition techniques has yielded highly oriented, crystalline organic films with carrier mobilities beyond 10 $cm^2 V^{-1} s^{-1}$ [8] contact issues turn out to be more complex. In this work we concern the improvement of metal-organic junctions in OFETs. Implemented as active layers organic π-conjugated molecules are intrinsic semiconductors. Injection properties are crucial, as OFETs switch between the accumulation and the depletion of injected charge carriers. At the metal – intrinsic organic semiconductor junctions neither ohmic contacts have been observed, nor clear indications for a Mott-Schottky limit have been shown. There is agreement that the charge injection is limited by significant contact barriers. Implemented in a device structure gold-pentacene junctions for example exhibit contact resistances in the range of MΩ [9,10]. An integration of OFETs to complex circuit arrays will cumulate the contact barrier effects, leading to high driving voltages, high threshold voltages and parasitic capacitances. Thus state-of-the-art organic electronic circuits are limited to operation in the kHz regime [4].

The work presented here targets the problem of barriers at metal–organic junctions. As discussed the energy level alignment at organic-metal interfaces is unfavorable for

* Corresponding author.
E-mail address: philipp@stadlers.ca (P. Stadler).

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injection. In particular the frequently studied pentacene-gold interface exhibits a significant barrier for holes [11,12]. The energy offset varies between 0.5 and 0.9 eV [13]. In order to reduce them the energy alignment at contacts has to be optimized. One strategy is to apply thin organic interlayers, for instance self assembled molecules (SAMs), which selectively attach to the contact metal. It has been demonstrated that SAM treatment enhances the transistor currents [8,14] and that the energy levels can be tuned towards a more favorable situation for injection [15].

In this work we introduce electrochemical contact doping as a novel strategy to improve metal-organic contacts. Here the hole injection is enhanced by electrochemically treating as-prepared OFETs. The approach tends to a p-doping of organic molecules adjacent to the injection electrodes. The goal is to create a *metal* to *doped* to *intrinsic* junction (metal-p-i junction). P-doping pins the Fermi level to the contact metal forming a narrow Schottky-junction and an improvement of hole injection [16].

The crucial part is to selectively p-dope molecules just in the vicinity of the electrodes. Molecules in the channel must not be affected. Electrochemical doping particularly satisfies this requirement, as it impacts the proximate electrode surrounding solely. Thus contact-doped OFETs render a MOSFET-related structure, where the source-drain electrodes face a narrow heavily p-doped semiconductor layer. The OFET channel itself is unaffected by the treatment. The metal-p-i junction is evoked by applying electrochemical doping directly to an as-prepared pentacene FET. We control the p-doping concentration by a profound electrochemical study. All parameters for creating the metal-p-i junction are presented chronologically step-by-step starting from electrochemistry and the contact doping followed by the transistor characteristics and finally a careful analysis of the contact resistance.

2. Experimental

Bottom-gate/top-contact (staggered) OFETs were used for a complementary study. We chose materials with high performance and good resistibility against electrochemical treatment. Aluminium deposited by vacuum deposition on a glass substrate served as gate electrode. For the gate dielectric 30 nm alumina was grown by anodic oxidation. The oxide was covered with divinyltetramethyldisiloxane – bis(benzo-cyclobutene) (BCB, Dow Chemicals). The cross-linked resin is fabricated by spin coating from a 1 wt.% precursor solution in mesitylene at 1500 rpm followed by an annealling step at 180 °C. The resulting hybrid dielectric has a geometric capacitance of 55 nF cm^{-2} [17]. Anodic alumina has excellent properties in terms of high dielectric breakdown fields [18–20]. BCB is applied for reducing shallow traps, for enhancing surface properties and for its thermal and chemical stability [21]. For the semiconductor 50 nm of pentacene (Aldrich) were applied by thermal evaporation at a constant substrate temperature of 50 °C during deposition and a rate of 0.4 Å s^{-1}. Gold source/drain contacts of 80 nm thickness were evaporated using a shadow mask with a channel width of 1 mm and a channel length varying from 40–120 μm.

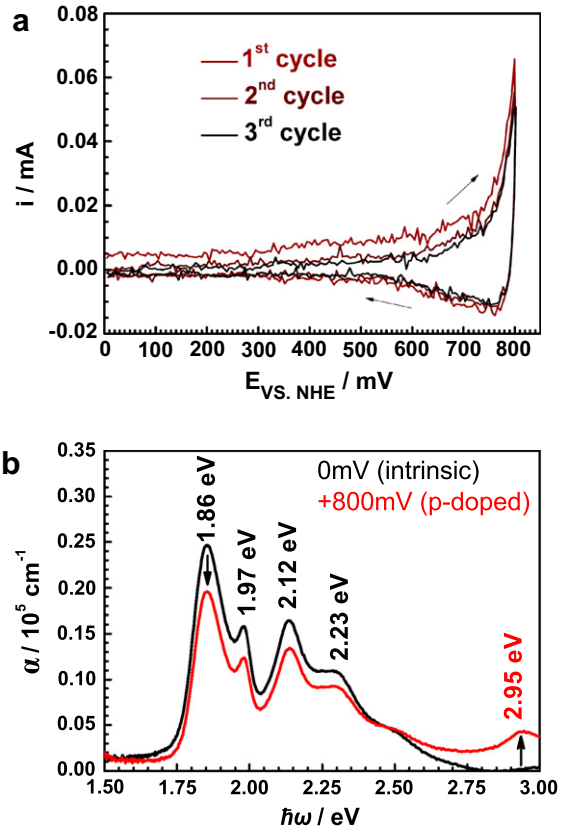

Fig. 1. (a) Cyclic voltammogram (CV) showing the reversible p-doping of pentacene thin film on ITO. (b) In-situ absorption recorded for intrinsic (black) and p-doped (red) pentacene. A new feature arises at 2.95 eV and the intensity of the four characteristic absorption features decrease. The relative drop in intensity is proportional to a p-doping concentration of approximately 1%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

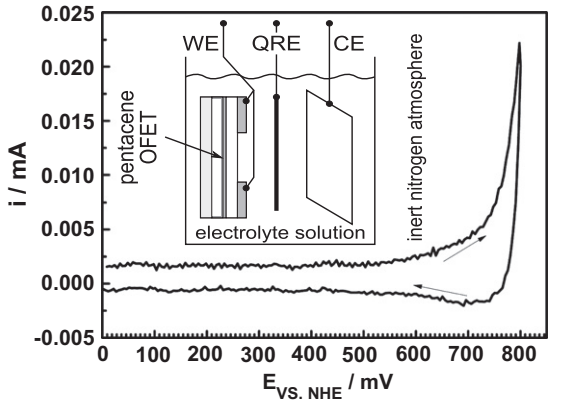

Fig. 2. Applying electrochemical contact doping to an OFET: Cyclic voltammogram showing the p-doping of pentacene recorded on an as prepared transistor. The inset shows the schematic of the setup, where source/drain electrodes in the staggered OFET act as the working electrode.

The electrochemical treatment and the electrical characterization were performed under nitrogen atmosphere, for the electrolyte solution an aprotic system was used

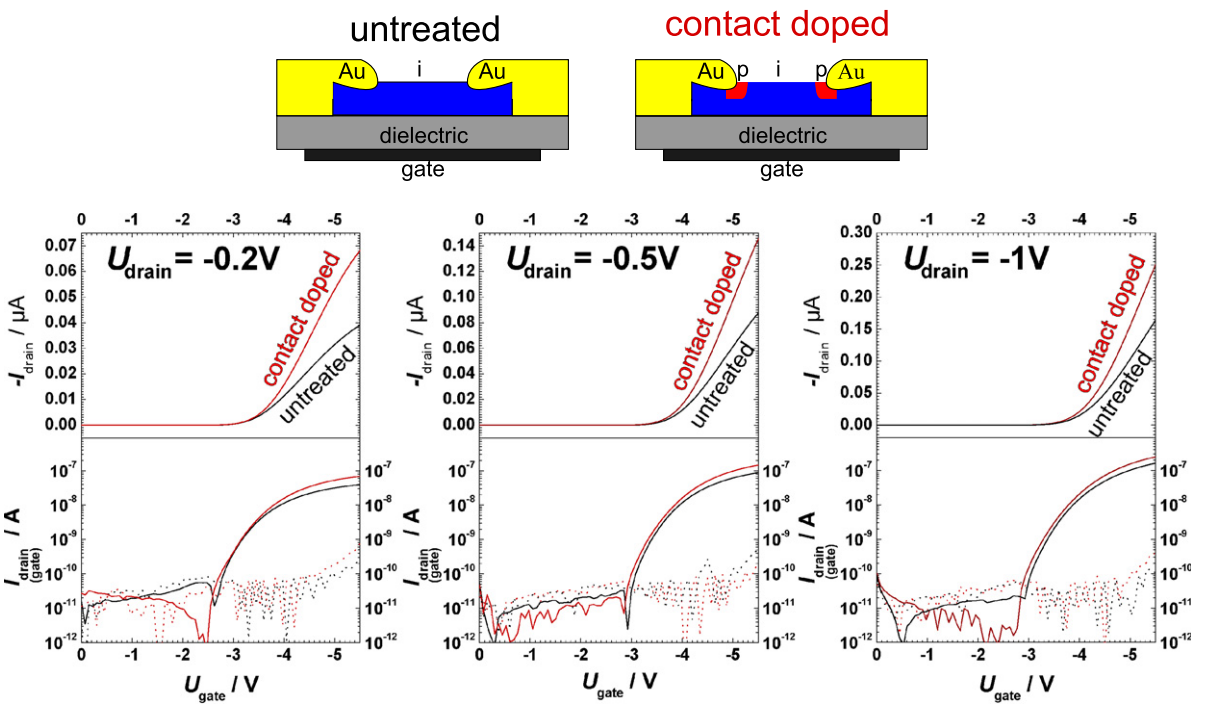

Fig. 3. Transfer characteristics of pentacene FETs (L = 40 µm) measured at different drain voltages (U_D=0.2 V, 0.5 V and 1 V) for untreated (black line) and electrochemically contact-doped (red line) OFETs. Concomitantly the drain currents and on/off ratios are enhanced after evoking the metal-p-i junction. The off-currents (semi-log plot) remain close to the detection limit at 10pA supporting that contact doping is limited to pentacene adjacent to the metal, while channel pentacene remains intrinsic as illustrated in the schematic on top. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(tetrabutylammonium hexafluorophosphate, $TBAPF_6$, Fluka, 99% dissolved in acetonitrile, Merck, 99.9%). All electrochemical parameters were studied from multiple voltammetric scans in a conventional three-electrode compartment cell. One cell was designed in a cuvette for performing in situ absorption spectroscopy in transmission mode. For that purpose pentacene films were deposited on glass/ITO. The contact p-doping for improving the injection properties was applied to the as-prepared transistor, where the gold source-drain electrodes served as working electrodes. The contact doping cell is depicted in the inset of Fig. 2. As counter and reference electrodes we used platinum and a Ag/AgCl rod respectively. The applied potential was controlled with a computerized electrochemical system and a potentiostat Jaissle 1030 PC.T. The reference electrode was calibrated versus a ferrocene/ferrocenium redox couple and showed a redox potential of 350 mV versus NHE.

3. Results and discussion

Prior the electrochemical treatment of the OFET the p-doping of a pentacene thin film was studied using cyclic voltammetry combined with absorption spectroscopy. We highlight the careful choice of the electrochemical p-doping potential. From previously reported electrochemical data on pentacene irreversible reactions start occurring beyond +800 mV destroying sigma bonds and the molecular backbone of the molecule [22]. Additionally, organic systems are known for overdoping effects, which is assigned to the disorder introduced by molecular dopants [23,24]. Therefore the potential window is limited between 0 and +800 mV.

The cyclic voltammograms (CVs) and the corresponding absorption spectra are presented in Fig. 1. Tracking the forward scans the oxidation currents start to increase at +600 mV followed by a steep rise beyond +700 mV. The reduction peaks in the back-scan are smeared out with a maximum between +700 to +600 mV. The integration of the CV yields approximately 1% of p-doping in the adjacent pentacene layer next to the electrodes. This doping level is confirmed by the in situ recorded spectra Fig. 1(b), which illustrate changes in the absorption features during doping. A p-doping induced decrease of characteristic pentacene bands is observed together with a concomitant rise of a new feature at 2.95 eV (indicated by arrows). We interpret the changes as a transfer of pentacene from the intrinsic to the p-doped radical cationic form [25]. The drops in relative intensity plus the CVs give us evidence of a significant and reversible p-doping of 1% at +800 mV.

The defined electrochemical treatment is then applied to an as-prepared OFET. A schematic of the setup and the CV is shown in Fig. 2. We denote that the voltammogram remains qualitatively unchanged compared to Fig. 1(a).

For evoking the metal-p-i junction in transistor pentacene, just a single forward-scan to +800 mV is applied. For studying the effect of contact doping the performances

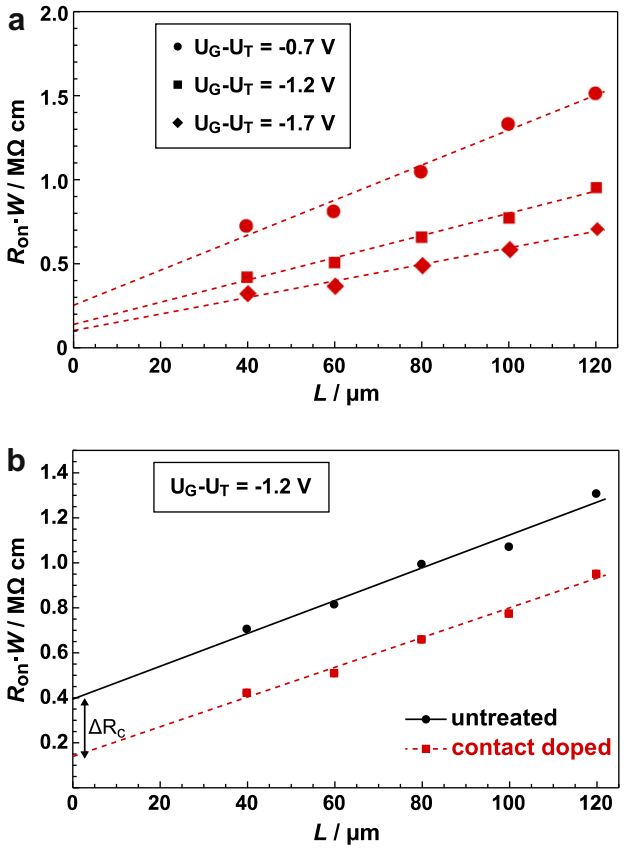

Fig. 4. (a) The transfer line method (TLM) measurement is presented for three different gate voltages on contact doped OFETs. (b) Change in the contact resistance of a pentacene FET before and after electrochemical treatment measured at a constant gate voltage of $(U_G - U_T) = -1.2$ V. Extrapolation to $L = 0$ yields the contact resistances R_c, which is reduced from 0.39 to 0.14 MΩ cm by contact doping.

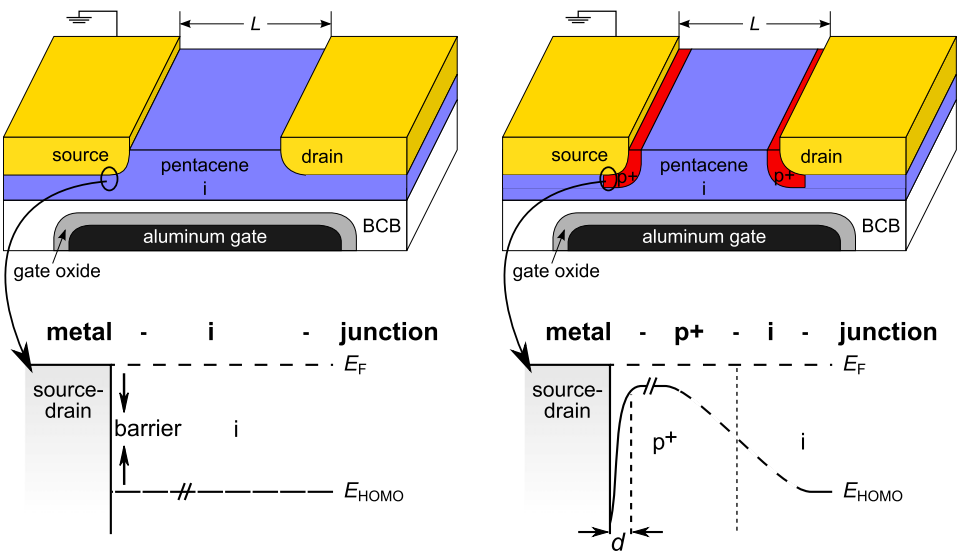

Fig. 5. Left: Schematic of untreated pentacene FET and energy picture of metal intrinsic semiconductor junction (metal-i-junction) with the contact barrier indicated below. Right: Schematic of contact doped pentacene FET, and changes of the energy levels introduced by contact doping: At the metal-p-i junction a Schottky-type contact enhances the carrier injection. p^+ denotes the doped and intrinsic pentacene. d is considered as the Schottky barrier width in the doped part adjacent to the interface.

of electrochemically untreated and treated OFETs are compared. The corresponding IV-curves are presented in Fig. 3. Throughout a number of different drain voltages the on-currents in the transistors are increased significantly. We assume a pure contact effect, since the off-currents in the transfer curve remain at the same level, which is seen in the semilogarithmic plots (solid lines). A careful analysis of the transfer curves reveals slightly reduced off-currents (range of 10 pA close to the setup detection limit). The increased drain currents and the reduced off-currents together support our assumption. Solely pentacene in the vicinity of the contacts is p-doped and the transistor operation is enhanced. We present further a selective investigation of the injection barriers using the transfer line method (TLM). The technique derives from MOSFET analysis to measure the contact resistance R_c [26,27]. It involves a number of transistors with different channel length L. The resistance is measured by recording the transfer characteristics in the linear regime at fixed drain potential $U_D = -0.5$ V. The threshold voltage U_T for every device is determined by the second derivative method and found consistently at around -4 V. The width-normalized total resistance $R_{on} \times W = U_D/I_D \times W$ is then calculated as a function of the gate voltage $(U_G - U_T)$. The total resistance R_{on} equals the series connection of the contact resistance R_c and the channel resistance, where the first term is assumed to be constant and the second term depends linearly on the channel length L, as given in Eq. (1),

$$R_{on} \times W = R_c \times W + \frac{L}{\mu \cdot C_i \cdot (U_G - U_T)}, \quad (1)$$

where μ is the hole mobility and C_i the geometric capacitance. By plotting the width-normalized total resistance for different channel lengths L and thereafter extrapolating linearly to $L = 0$ the contact resistance in dependence of gate voltage can be extracted.

An example of such a measurement is shown in Fig. 4 for contact doped devices. The extrapolation of the channel length yields different contact resistances. Similar to MOSFET structures the resistance is a function of the gate voltage and assigned to the gate-dependent doping gradient at the p-doped to intrinsic junction [28,29]. We choose a gate voltage of $((U_G - U_T) = -1.2$ V) for comparison of transistors with and without treatment. The contact resistance drops by 64% from initially 0.39 to 0.14 MΩ cm, equal to $\Delta R_c = 0.25$ MΩ cm. This observation is valid for any gate voltage within the measured interval.

Fig. 5 shows the energy diagrams of both the metal-i and metal-p-i junction respectively. Differently to the metal to intrinsic pentacene we derive a Schottky-type contact for the metal to p-doped pentacene junction. At significant p-doping concentrations we deduce a narrow barrier width d, plotted as the solid, asymptotic line next to the metal in the graph. In that case the width d would hardly exceed the range of the molecular size of pentacene. Further away from the contact we expect a gradual transition from p^+ to finally intrinsic pentacene deeper in the channel denoted by the dashed line. Compared to the metal-i junction with its characteristic barrier offset from the HOMO (indicated) the energy alignment for the electrochemically treated junction enables tunneling through the narrow Schottky-barrier for an efficient injection of holes. The tunneling process is in our opinion the origin for the enhanced performance. The results presented here support this picture as reflected in the schematic. A pronounced reduction of the hole barrier is indeed observed. The electrochemical treatment affects only the close surrounding of the injection electrode, which is confirmed by measuring the contact resistances on a representative number of OFETs. They drop more than 60% from their original values. Apart from the crucial role of the electrochemically created p^+ pentacene interlayer we stress that the residual channel region remains unaffected by the treatment. The increased on/off ratio backs this statement. Electrochemical p-doping may be applied to various organic devices for a contact improvement. As demonstrated here the device performance can be tailored towards the needs of organic electronic integrated circuits with low driving and threshold voltages and with minimum baseline parasitic capacitances. As pointed out contact barriers are the sore limiting factor in complementary organic circuits. Therefore we consider electrochemical contact doping as a pathway to work around the problem for increasing switching frequencies at low-level driving/threshold voltages.

4. Conclusions

The study here demonstrates the creation of a metal-p-i organic junction. The contact-limited electrochemical p-doping of pentacene reduces the contact resistance at the source-drain electrode by more than 60%. We report on a reduction of 0.25 MΩ cm. The implementation of electrochemical doping to an OFET structure is demonstrated by a study using cyclic voltammetry and in situ absorption spectroscopy. Based on the rich data-pool concerning electrochemical doping in π-conjugated systems we believe this strategy can be generally utilized in organic electronic devices for improving the metal–semiconductor interface.

Acknowledgments

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